

Kinetics and Mechanism of Sol-Gel Transformation between Sodium Alginate Anionic Polyelectrolyte and Some Alkaline Earth Metal Ions with Formation of Coordination Biopolymer Ionotropic Polymembrane Hydrogels of Capillary Structures

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Abstract

The kinetics of formation of coordination biopolymeric multimembranes hydrogels of capillary structure between Ca(II), Sr(II) and Ba(II) metal ions and sodium alginate sol as a polysaccharide has been studied complexometrically at various temperatures. When the alginate sol was present in large excess over that of the metal ion concentration, the pseudo-first-order plots of sol-gel transformation showed sigmoidal curves of two distinct stages. The first stage was relatively fast, followed by a very slow stage at longer time periods. The rate-law of gel formation was described by the form $(C_t - C_\infty) = B_0 e^{-k_f t} + P_0 e^{-k_s t}$, whereas the two gelation pathways showed a simple first-order dependence with respect to both the metal ion and alginate sol. The kinetic parameters have been evaluated and a gelation mechanism consistent with the kinetic results has been suggested.

Keywords

Biomaterials; Membranes; Gelation; Kinetics; Biocatalysts; Hydrogels; Alginates

Introduction

Alginic acid is a binary heteropolymer polysaccharide compromising (1-4) β -D-mannuronic and α -L-guluronic acid units (Chanda et al.; Whistler et al.; Fischer et al.). The monomers are arranged in a blockwise structure along the macromolecular chains (Smidsrod et al.). Alginates show a high affinity for

chelation with polyvalent metal cations in particular with divalent metal ions forming their coordination biopolymer cross-linked metal-alginate hydrogels (Smidsrod et al.; Thiele et al.). The sol-gel transformation process takes place by a stepwise replacement of sodium counter ions, Na^+ , of alginate macromolecule by polyvalent metal cations. These ionotropic hydrogels can be found in different shapes and various morphologies depending on the apparatus used and the direction of diffusion of the metal ion electrolyte toward the alginate sol, respectively (Thiele et al.; Hassan et al.).

These polymeric biomaterial hydrogels in particularly metal-alginate membranes are widely used in many potential applications in chromatographic separation (Hassan et al.) for the removal of toxic heavy metal cations and radionuclides from contaminated matters such as seawater and environment (Mimura et al.). Their sphere and bead shape hydrogels can be used as biocatalysts in immobilization systems (Smidsrod et al.) such as drug delivery, tissues engineering, medical adhesion (Shaha et al.), ethanol manufacturing (Torres et al.) and in ultrafiltrations purposes (Hassan et al.). However, a little attention has been focused on the kinetics of sol-gel transformation processes. Even though, the kinetics of gelation for cross-linked

copper-alginate hydrogel spheres was investigated for the first time (Awad et al.).

In view of the above aspects, the present work has been undertaken as part of a series of investigations on the kinetics of gelation processes between the alginate as an anionic polyelectrolyte and some divalent metal ions (Awad et al.; Hassan et al.; Khairou et al.) with the aims to shed highlight on the kinetics of gelation and to elucidate a suitable gelation mechanism. The results revealed knowledge on the stability of these ionotropic hydrogel complexes with much attention to the influence of the nature of metal ions, strength of chelation and coordination geometry on the complex stability

Experimental

Sodium alginate used was Cica-Reagent (Kanto Chem. Co.). The degree of substitution was found to be 4.34 mmol g⁻¹ (0.95 molmol⁻¹). The measured viscosities using an Ubbelhode viscometer for a 4% alginate sol in water at 20°C were found to be 2.78 and 9.87 dl g⁻¹ for the inherent and reduced viscosities, respectively.

All other materials were of analytical reagent grade. Doubly distilled conductivity water was used in all preparations. The temperature was controlled within $\pm 0.1^{\circ}\text{C}$.

The electrolyte solutions of the divalent metal ions and sols of sodium alginate of various concentrations were prepared and standardized as described elsewhere (Awad et al.; Hassan et al.; Khairou et al.).

Kinetic Measurements

Preliminary experiments indicated that the rate constants of such sol-gel transformation were altered on changing the concentration of either metal ion or the alginate sol. From this point of view, the kinetics of the present study were performed under pseudo-first-order condition where $[\text{Alg}]_0 \geq [\text{M}^{2+}]_0$. The procedure of the kinetic measurements was the same as described earlier (Awad et al.; Hassan et al.; Khairou et al.). One-closed side columns of 3-5 cm diameter and 10 cm in height were used. The columns were internally smeared with a very thin layer of the alginate sol to be used in order to form an adhesive thin layer membrane of alginate within the internal walls of the column. This thin layer will prevent any deterioration of the alginate sol placed into the columns used during addition of an electrolyte solution over the alginate sol surface as well as during

the exchange process. These columns are dried in an electric oven at 105°C for about 20 min, and then cooled at room temperature.

Each column was filled to about one-third of its height with alginate sol of known concentration. Then, the column and the electrolyte solution of the metal ions were equilibrated at the desired temperature in a thermostated water-bath. After the reactants have attained the temperature of the water-bath, a fixed volume of the metal ion electrolyte solution of known concentration was carefully poured into the column containing the alginate sol until it reached about two-thirds of its height using a syringe or a pipette. The addition of the electrolyte solution was performed in such a way to avoid any mixing of the two liquid phases, the alginate sol and the metal ion electrolyte. The time of contact of the metal ion electrolyte with the sol surface was recorded. After known time intervals, known volumes of the electrolyte solution were pipetted out and the variation of concentration as a function of time was followed complexometrically (Vogel; Schwarzenbach et al.). Before taking the sample for analysis, a smooth current of air was gently bubbled in the electrolyte solution to avoid the concentration gradient resulting from the exchange process of the counter ions across the primary membrane which was fastly formed between the electrolyte solution and the alginate sol.

It was noticed that the observed rate constants of gelation were decreased with the increasing alginate sol concentration beyond $[\text{Alg}]_0 \geq 0.15 \text{ mol dm}^{-3}$. This may be explained by the marked increase of alginate viscosity with increasing its concentration, which in turn may tend to retard the mobilities of the two exchanging counter ions. This means that the exchange process is delayed and, hence, a decrease in the observed rate constant of gelation must occur as experimentally observed. Therefore, all of the experimental runs in the present work were performed under the conditions of $[\text{Alg}]_0 \leq 0.15 \text{ mol dm}^{-3}$ (~3 % alginate sol). The results are an average of at least five experimental runs for each.

Results

Stoichiometry

Ion exchange is inherently a stoichiometric process (Hellferich; Haugh et al.), meaning that the Na^+ counter ions, resulting from the dissociation of sodium alginate sol, which leave the macromolecular chains of alginate

polyelectrolyte must be replaced by an equivalent amount of the added divalent metal ions even the valencies and mobilities of the two counter ions may be quite different. The stoichiometry of the overall gelation reaction was determined complexometrically in the presence of a slightly known excess metal ion concentration over that of the alginate one as described earlier (Hassan; Khairou et al.). No specific method was found to determine the concentration of alginate sol. Stoichiometric ratios of 0.55 ± 0.05 ($[M^{2+}]_{\text{consumed}}/[Alg]_0$) were obtained at several initial concentrations of metal ions. This result conforms to the following stoichiometric equation



where Na-Alg denotes sodium alginate, M-Alg₂ is the metal alginate hydrogel complex and M is the metal ion.

Reaction-time Curves

The reaction-time curves were found to be of sigmoidal shape. The initial rates were relatively fast in the early stages, followed by a decrease in the reaction rates at longer time periods. Two definite slopes of linear plots are recognized as shown in Fig. 1. These curves indicate that the gelation reaction obeys the expression

$$(C_t - C_\infty) = B_0 e^{-k_f t} + P_0 e^{-k_s t} \quad (2)$$

where k_f and k_s are the observed pseudo-first-order rate constants of gelation for the fast and slow steps, B_0 and P_0 represent the initial concentration of the sol in the two gelation processes and C_t and C_∞ are the concentration of the metal ion at times t and infinity, respectively. The analysis is the same as described earlier (Awad et al.; Hassan et al.; Khairou et al.)

Dependence of Rate Constants of Gelation on $[Alg]$ and $[M^{2+}]$

The order with respect to the reactants was determined by working under pseudo-first-order conditions where $[Alg]$ was present in a large excess over that of metal ion electrolyte. The present work is concerned with the fast initial parts, since the second stages are too slow. The second-order rate constants of gelation, R_g , were obtained by dividing the observed first-order rate constants, k_f or k_s by the initial alginate concentration ($R_g = k_f$ or $(k_s) / [Alg]_0$). The constancy obtained indicates that the rate constants of gelation are also first-order in alginate concentration. The rate constants of gelation calculated by the method of least-squares are summarized in Tables 1 and 2.

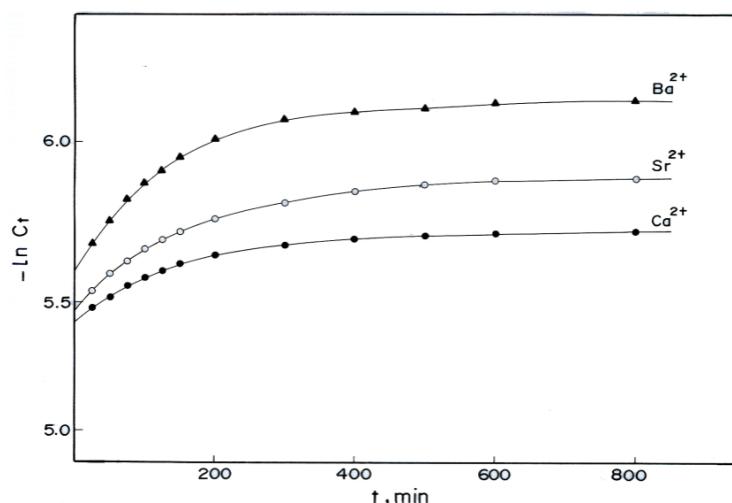


FIG. 1 TYPICAL PSEUDO-FIRST-ORDER PLOTS FOR GELATION REACTION. $[ALG] = 5 \times 10^{-2}$ MOL DM⁻³, $[M^{2+}] = 4 \times 10^{-3}$ MOL DM⁻³ AT 25°C

TABLE 1 THE OBSERVED FIRST-ORDER RATE CONSTANTS OF GELATION, $[ALG]_0 = 5 \times 10^{-1}$ MOL DM⁻³, $[M^{2+}] = 4 \times 10^{-3}$ MOL DM⁻³ AT 35°C

Metal ion Rate	Ca ²⁺		Sr ²⁺		Ba ²⁺	
	$10^5 k_{\text{obs}}$, s ⁻¹	k	k	k	k	k
		0.89	0.19	1.63	0.36	2.28
						0.94

TABLE 2 THE SECOND-ORDER RATE CONSTANT OF GELATION. $[M^{2+}] = 4 \times 10^{-3}$ MOL DM⁻³ AT 45°C

$10^2 [Alg]_0$, M	Ca ²⁺		Sr ²⁺		Ba ²⁺	
	$10^5 k_f$, s ⁻¹	$10^4 R_g$, dm ³ mol ⁻¹ s ⁻¹	$10^5 k_f$, s ⁻¹	$10^4 R_g$, dm ³ mol ⁻¹ s ⁻¹	$10^5 k_f$, s ⁻¹	$10^4 R_g$, dm ³ mol ⁻¹ s ⁻¹
2.53	0.53	2.10	0.99	3.91	1.37	5.41
5.05	1.04	2.05	2.01	3.98	2.74	5.43
7.58	1.58	2.09	3.02	3.99	4.06	5.36
10.10	2.03	2.01	3.94	3.90	5.35	5.30

TABLE 3 KINETIC PARAMETERS AND THE SECOND-ORDER RATE CONSTANTS OF GELATION (AT 25°C) FOR SOME SOL-GEL TRANSFORMATION REACTIONS BETWEEN METAL CATIONS AND ALGINATE MACROMOLECULE (INITIAL AUTO- ACCELERATION STAGE)

Metal alginate	104 Rg, dm ³ mol ⁻¹ s ⁻¹	E ^{#a} kJ mol ⁻¹	ΔS [#] JK ⁻¹ mol ⁻¹	ΔH [#] kJ mol ⁻¹	ΔG ^{#298} kJ mol ⁻¹	Reference
Ni ²⁺	3.90	29.83	-244.89	25.29	92.19	Hassan et al.
Cu ²⁺	3.55	15.73	-176.64	37.80	90.44	Hassan et al.
Co ²⁺	8.28	28.69	-260.89	14.77	92.50	Hassan et al.
Sn ²⁺	9.12	16.25	-257.76	13.56	90.37	Hassan et al.
Hg ²⁺	1.99	12.62	-285.99	8.72	93.49	Hassan et al.
Zn ²⁺	0.83	27.50	-240.09	24.79	96.34	Hassan et al.
Cd ²⁺	1.58	62.99	-116.56	60.34	95.68	Hassan et al.
Pb ²⁺	3.03	24.46	-258.29	21.80	92.81	Hassan et al.
Ca ²⁺	1.54	11.49	-288.25	8.86	94.75	This work
Sr ²⁺	2.77	16.97	-265.62	14.29	93.44	This work
Ba ²⁺	3.78	12.59	-260.85	12.59	90.52	This work

Experimental errors ± 4%

Dependence of Rate Constants of Gelation on Temperature

The kinetic parameters of gelation processes were determined from the temperature-dependence of the rate constants for the initial fast stage using the Eyring's equation (Glasstone et al.). These parameters calculated using the least-squares method are summarized in Table 3, along with the kinetic parameters for other gelation reactions

Discussion

When the electrolyte solution of a divalent metal ion comes in contact with the alginate sol, a very thin primary membrane will be rapidly formed on the surface of the alginate sol. This membrane will separate the alginate sol from the surrounding electrolyte, whereas the macromolecular chains of alginate polyelectrolyte starts to distribute themselves statically below the already formed primary membrane. As a steady-state condition has been established, the Na⁺ counter ions produced from the dissociation of the alginate sol macromolecule began to diffuse themselves from the alginate sol outward into the electrolyte solution through the primary membrane. Simultaneously, the metal ions of the electrolyte solution must migrate inward in order to occupy the places left by Na⁺ ions from the alginate macromolecule. The net process is a transfer of ions in both the sol and the electrolyte phases (Awad et al.; Hassan et al.; Khairou et al.).

The interdiffused metal ions tend to chelate the carboxylate and hydroxyl functional groups of the alginate macromolecule. This chelation is not just simple, but a sort of bridge between the metal ion and two carboxylate and one or more pairs of the hydroxyl

groups occurs through partially ionic and partially coordinate bonds, respectively. The number of chelated OH groups depends on the coordination number of the interdiffused chelated metal ion. This chelation leads to the formation of coordination biopolymer ionotropic gel complexes in an egg-carton like structure (Perry et al.; Rees et al.; Braccini et al.; Schweiger). Therefore, two geometrical structures for such chelation may be suggested (Hassan). The first one corresponds to an intramolecular association in which the functional groups involved in chelation belong to the same chains. Hence, the symmetry plane of the gel complex involving the chelated metal ion is parallel with the plane of the alginate macromolecular chains and can be represented by planar geometry. The second type of geometry is termed non-planar geometry and corresponds to the intermolecular association. Here, the plane containing the metal ion is perpendicular to the plane of alginate macromolecular chains, i.e. the carboxylate and hydroxyl functional groups are realted to different chains. The priority of the two geometrical structure depends on the nature of the metal ion and its valency. The two configurations are shown in Scheme 1.

When the metal ions are allowed to diffuse upward, non-capillary gel membranes are formed. This method of gel preparation is known as the ascending technique. On the other hand, when the metal ions diffuse in the downward direction, the method of gel preparation is termed as the descending technique. The sol-gel transformation of ionotropic gels is usually accompanied by the formation of capillaries in the direction of diffusion between the two counter ions. These capillaries are straight, parallel and nearly identical to each other. Under microscopic investigations, these capillaries appear as fine pores of the same radius in a traverse section (Hassan) as

shown in Fig. 2. The dehydration of solvent water molecules from the polymembrane gels gives

transparent film of homogeneity. The capillaries in this film appear to be spiral or cone shaped

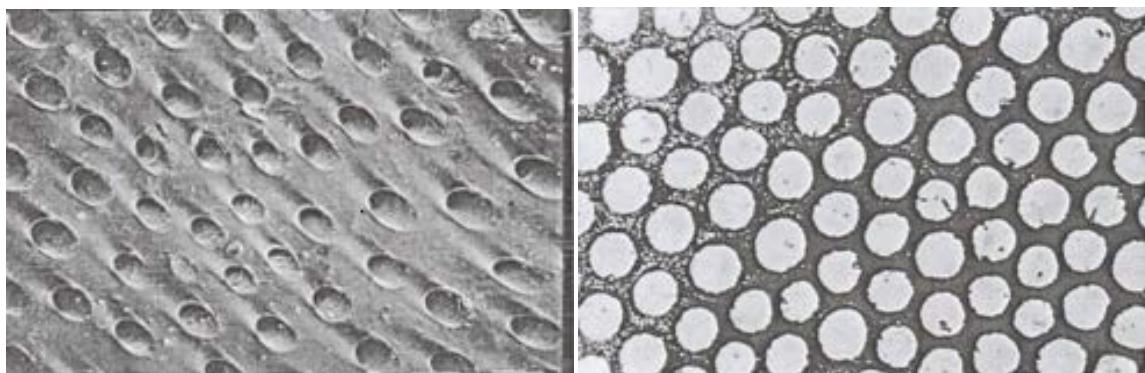
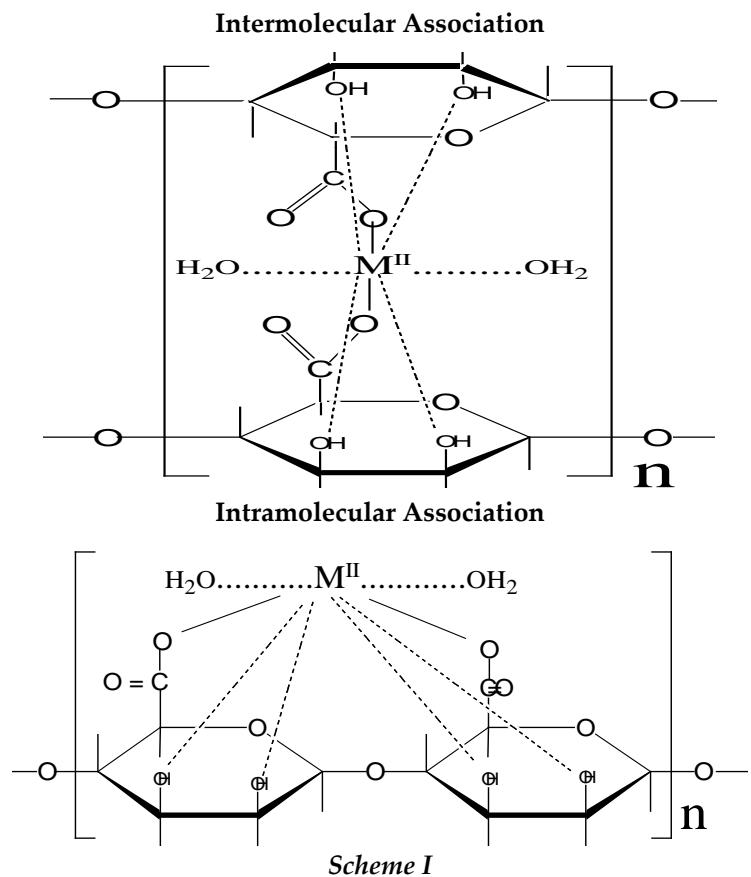


FIG. 2 OPTICAL IMAGES OF TRANSVERSE SECTIONS IN CROSS-LINKED CALCIUM (II)- ALGINATE COMPLEX

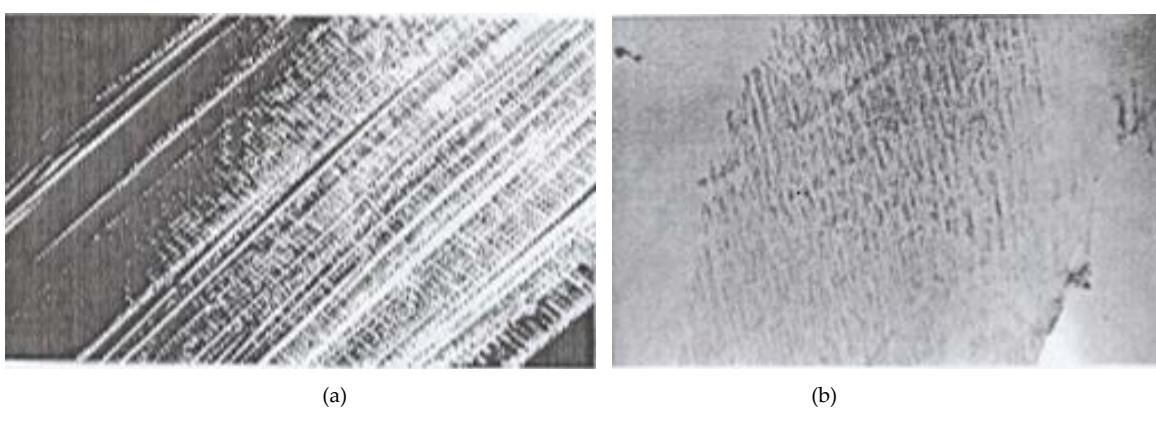


FIG. 3 (a) SEM AND (b) TEM IMAGES IN CROSS-LINKED CALCIUM (II)-ALGINATE COMPLEX

The diameter of these pores depends on several factors such as pH of electrolyte, concentration of alginate sol, the ionic radii of the interdiffused metal ion and the orientation of the coordinated water molecules and the chains of alginate macromolecule toward the chelated metal ion (Hassan et al.)

The pore size in these membranes could be controlled by changing the pH of the alginate sol on addition of certain electrolytes. These polymembranes can be applied in ultrafiltration (Hassan et al.) and in other analytical purposes such as chromatographic separation (Smidsrod et al.; Shaha et al.; Torres et al.; Hassan; Awad et al.). The width of these capillaries will play an important role in the rate of exchange process for sol-gel transformation processes. The diffusion process takes place stepwise and the continuity of such diffusion will lead to the formation of multilayer ionotropic membranes. It is possible to separate those multilayers into thin layer membranes as shown in Fig. 3. These thin layers can be used in electrophoto conductography as cellular reinforcement screens for X-rays and photographing the electron beams of oscilloscopes.

The rate of gel formation was noticed to be greater at the initial stages and, hence, it gradually decreased at longer times. This means that the rate of ion exchange between the exchanging counter ions, Na^+ and metal ions, is much larger at the moment of contact of the metal ion with the alginate sol, then, it decreased and that decrease became almost constant. The relatively fast initial part is explained by the formation of

primary gel membrane. The second slow part seems to be controlled by the compactness of the network of the already formed gel membrane, which depends on several factors such as the concentration of alginate sol and temperature.

Generally, two possible rate-determining steps in ion exchange reactions may be considered. They are the counter ion exchange across the interface between the alginate sol and the metal ion electrolyte [Perry et al.,] and the actual exchange of the fixed ionic groups (Dickel et al.; Tetenboum et al.). Rate control by ion exchange across the interface is unlikely (Richman et al.). Therefore, it is worthwhile to consider the exchange of the interdiffused metal ions in either fast or slow gelation steps as the rate-controlling step. The values of the activation energy obtained may support this suggestion (Table 3)

As shown in Table 2, the rate constants of gelation are increased in the order Ca^+ < Sr^+ < Ba^+ -alginates. The magnitude of the rate constants is mainly dependent on the ionic radii of the interdiffused metal ions. As shown in Fig. 4, a plot of $\ln R_g$ versus the ionic radii is found to be fairly linear. Barium (II) is the largest (Cotton et al.) and, hence, it has the greatest rate. Whereas calcium (II) is the smallest and, hence, it should have the lowest rate as experimentally observed. Also the density of the metal ion electrolyte which depends on the atomic weight of the metal ion may play a role in the kinetics of gelation. A plot of $\ln R_g$ vs \sqrt{Z} (where Z is the atomic number) is also linear as shown in Fig. 5.

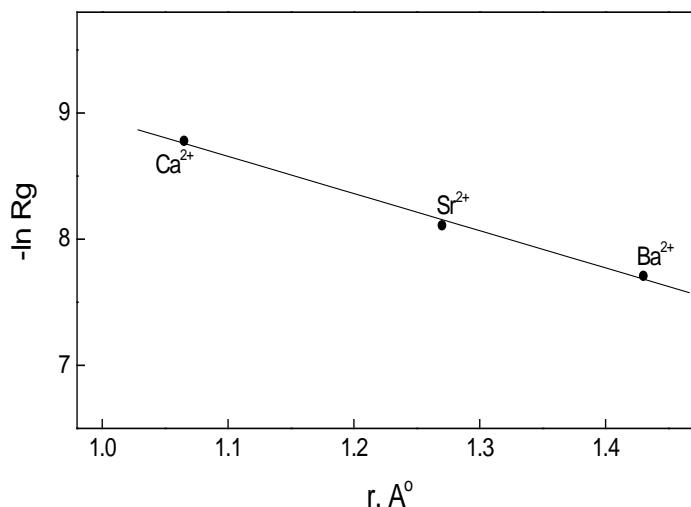


FIG. 4 DEPENDENCE OF GELATION RATE ON IONIC RADII $[\text{ALG}] = 5 \times 10^{-2}$ MOL DM^{-3} , $[\text{M}^{2+}] = 4 \times 10^{-3}$ MOL DM^{-3} AT 25 °C

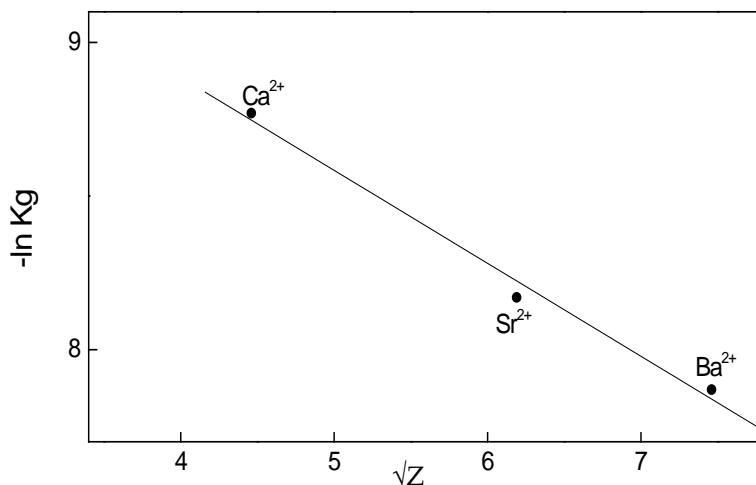


FIG. 5 DEPENDENCE OF GELATION RATE ON ATOMIC NUMBER [ALG] = 5X10⁻² MOL DM⁻³, [M²⁺] = 4X10⁻³ MOL DM⁻³ AT 25°C

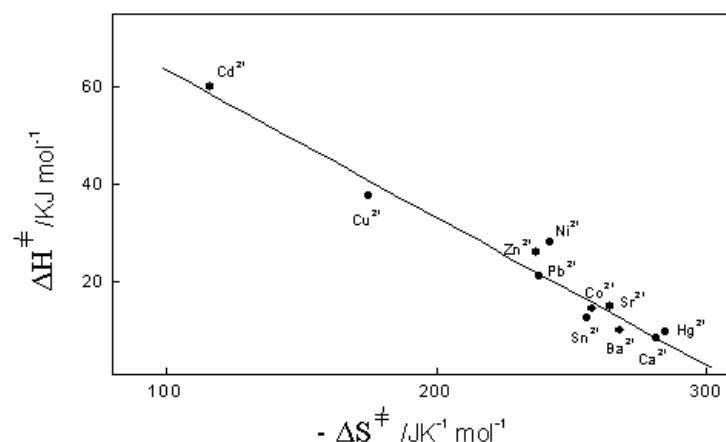


FIG. 6 ISOKINETIC RELATIONSHIP FOR SOME GELATION REACTIONS FOR THE INITIAL FAST STAGE

Furthermore, the large negative entropy of activation observed in Table 3 can be explained by the necessity of the small metal ions to penetrate the large carboxylate groups in order to bring them together to form coordination biopolymer ionotropic gel complexes of polymembrane nature. It was found that the orientation of the macromolecular chains and the solvent molecules toward the chelated metal ions strongly affected the kinetic parameters of sol-gel transformation, and, hence, it tended to influence the entropy of activation (Awad et al.; Hassan et al.; Khairou et al.). Since the entropy of activation decreases with increasing orientation factor, the magnitude of orientation should be in the order $\text{Ca}^2+ > \text{Sr}^2+ > \text{Ba}^2+$ (Thiele et al.; Thiele et al.). This is in good consistent with the values of entropies of activation observed for these metal-gel complexes.

The activation energies observed in Table 3 indicate that stability decreases in the order $\text{Sr}^2+ < \text{Ba}^2+ \leq \text{Ca}^2+$.

alginate complexes. Again, despite of the variety of metal ions used, it seems that the free-energy of activations remains unaltered (Table 3). This fact may suggest a similarity of gelation mechanisms between these metal ions and alginate macromolecule. Hence, the nature of the metal ions and the geometrical configurations play the main role in the magnitude of the gelation rates. Leffler and Grunwald (Leffler et al.) have pointed out that many reactions may show isokinetic relationship given by $\Delta H^\ddagger = C + \beta \Delta S^\ddagger$. As shown in Fig. 6, a plot of ΔH^\ddagger versus ΔS^\ddagger for these gelation reactions is fairly linear with $C = 94 \text{ kJ mol}^{-1}$ and $\beta = 305 \text{ K}$. This linearity may also confirm that the ion exchange processes in these gelation reactions follow similar sol-gel transformation mechanisms.

Conclusion

The replacement of Na^+ counter ions of alginate polysaccharide sol as anionic polyelectrolyte by

divalent metal ions leads to the formation of coordination biopolymeric metal alginate ionotropic hydrogel complexes. This process takes place by fast formation of a thin primary membrane, followed by slow diffusion process between the exchangeable counter ions. The formed hydrogel complexes are characterized by distinct morphological structures depending on the direction of diffusion between the exchangeable counter ions, nature and concentration of the interdiffused metal ion and the alginate sol.

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